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PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO BRAZING ALUMINIUM

(71) We, ALCAN RESEARCH AND DEVELOPMENT LIMITED, a Company incorporated under the laws of Canada, of 1, Place Ville Marie, Montreal, Quebec, Canada, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to methods of joining aluminium (including aluminium alloys) by brazing.

It is already known to join aluminium components by melting an aluminium brazing alloy between or adjacent the faying surfaces (i.e. the surfaces to be joined, in the presence of a flux, which dissolves or disrupts the aluminium oxide film on the metal surfaces. It is commonly preferred that the melting point of the brazing alloy be at least 30° to 40°C lower than that of the metal of the components. An example of a suitable brazing alloy is an Al-Si eutectic composition, which melts at about 577°C and thus melts at a temperature which is at least 30°C below the melting point of aluminium and most commonly used aluminium alloys.

Although it is normal practice for at least one component to be made from brazing sheet (aluminium alloy clad with aluminium brazing alloy), it is also known to apply the brazing alloy as a powder, carried in a suitable liquid or paste-like vehicle.

Fluxless aluminium brazing is known which requires to be performed at sub-atmospheric pressure and is therefore expensive and inconvenient. Other fluxless methods, which require the use of an inert atmosphere at atmospheric pressure, are also known, but these are highly sensitive to even trace amounts of oxygen and water vapour contamination of the atmosphere and are likewise expensive and inconvenient to operate. It is, therefore, normal practice to employ a flux in brazing aluminium to remove the oxide film

ordinarily present on aluminium surfaces. The material used as a flux must be capable of dissolving or disrupting aluminium oxide at the brazing temperatures while remaining inert with respect to aluminium at such temperatures. 50

It has been usual to employ mixtures of metal chlorides as fluxes for brazing aluminium. These fluxes are water-soluble and usually hydroscopic and are corrosive to aluminium (including aluminium brazing alloys) in the presence of water; hence residues of such fluxes must be removed by washing at the end of the brazing operation. 55

It has already been proposed to use a mixture of a powdered brazing alloy with chloride flux in a suitable liquid vehicle. The required vehicle has thus been limited to organic liquids in which the chloride-containing flux does not attack the brazing alloy particles. Because the fluxes are hydroscopic, this expedient has not been satisfactory, since it has been necessary to proceed with the brazing operation as soon as the vehicle had dried. 60

We have already described in Patent No 1,438,955 aluminium brazing fluxed consisting of one or more potassium fluoaluminate complexes (either KAlF₄ alone or in admixture with K₂AlF₆) and essentially free of unreacted potassium fluoride. These fluxes are non-hydroscopic and leave no water-soluble residue. Such fluxes are reactive at temperatures above 560°C to strip from or dissolve oxides on aluminium surfaces but are essentially inert with respect to metallic aluminium so that there is no necessity to wash a brazed assembly to remove flux residue for avoiding corrosion. 65

The present invention provides a method of joining aluminium components by means of an aluminium brazing alloy having a melting point lower than that of the aluminium components, in which the assembled components are heated to a temperature above the melting point of the brazing alloy and below the melting point of 70

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5 said components in the presence of a potassium fluoaluminate flux, which is essentially free of unreacted KF characterised in that the flux and the brazing alloy are applied to the surface of at least one of the components as an aqueous slurry of finely divided flux and metal powder, the film of slurry is then dried and the components are brazed (after assembly, if necessary) by heating in a dry, oxygen-free inert gas atmosphere, the application of flux/brazing alloy slurry being controlled to apply 30—180 gms/m² of solids and the flux: brazing alloy ratio being selected to deposit at least 3.29 gms/m² of flux.

10 We have now discovered that the said flux, consisting essentially of potassium fluoaluminate, possibly with some unreacted AlF₃, but essentially free of unreacted potassium fluoride, may be maintained in an aqueous slurry with powdered aluminium brazing alloys for extended periods of time without deleteriously attacking the brazing alloy particles.

15 20 25 30 35 40 45 50 55 60 65 We have found, very surprisingly, that aluminium brazing alloy particles and flux particles may be deposited on aluminium from such slurry and be dried to form a film which has reasonable adhesion to the aluminium. By contrast, a slurry of aluminium brazing alloy particles alone does not form a film of adequate adhesion. In some circumstances as little as 2% flux in the total solids of the slurry is sufficient. More usually it is preferred that the flux should be present in an amount of 10—20% of the amount of the brazing alloy particles by weight. The weight of water in which the mixture of flux and metal powder is dispersed may be varied depending on the desired consistency of the dispersion, but is typically less than the weight of powder dispersed in it.

While the slurry may be applied by spraying or brushing, the most convenient procedure for high volume commercial production of brazed assemblies is to dip the components into the slurry before or after assembly. This leads to deposition of the slurry on all the available surfaces of the components. Surface effects lead to preferential deposition between faying surfaces when assembled components are dipped. The particle size of the flux and metal powder should both be less than 200 mesh (less than 75 microns) to ensure entry between the faying surfaces of assembled components.

By variation of the amount of water in the slurry and by control of other factors, particularly the rate of withdrawal of the component or assembly of components from the slurry, it is possible to deposit a slurry coating having a solids content of a few hundred gms/m² but an especially

useful range is 40—150 gms/m². Such coating after the necessary drying step has sufficient adhesion to the aluminium component to allow it to be handled. It is, of course, necessary to pretreat the surface to ensure that the surface has been adequately degreased to allow the slurry to wet the surface.

The thus deposited coatings of flux and brazing alloy powder may contain sufficient flux to permit the brazing to be carried out in the normal oxidising atmosphere of a brazing furnace. However, the quantity of flux required for such operation is so high that large quantities of unsightly flux residue result and furthermore the costs of the brazing operation are significantly increased. Therefore, as a further feature of the invention the brazing operation is performed in a furnace having an atmosphere of a dry inert gas. The atmosphere is commonly dry oxygen-free nitrogen, i.e. dried to a moisture content of less than 250 p.p.m. water vapour and having a free oxygen content of less than 3000 p.p.m. Other gases, which are inert to aluminium, such as cracked ammonia, may be employed provided that their free oxygen and moisture content are held down to the same levels. The furnace atmosphere is held at a temperature above the melting point of the powdered aluminium brazing alloy and of the flux, but below that of the aluminium or aluminium alloy components, which are to be joined by the brazing operation. This brazing procedure is satisfactory for almost all aluminium alloys which have a solidus temperature above the liquidus temperature of the brazing alloy. However, the flux provides less satisfactory results when the components to be joined (or one of them) has a Mg content in excess of 1%.

As already explained, the flux/brazing alloy ratio of the slurry may be varied through quite wide limits. It is, however, usually satisfactory to operate the process with a flux content of 5—15 gm/m² in the dried film. Thus the ratio of powdered brazing alloy filler metal and water to flux will preferably be arranged so as to deposit a desired coating weight of brazing alloy in conjunction with a flux content in the stated range. There is no upper limit for the amount of flux from the point of view of forming an effecting joint. However, the appearance of the work is marred by heavy fused flux residues and therefore it is preferred to restrict the flux to not more than 50 gms/m².

The powdered brazing alloy/flux slurry may incorporate suspension agents and corrosion inhibitors, but these do not appear to be necessary in any operation where the dwell time of the slurry in the

- bath is of limited duration. Small quantities of surface active agents may be included to assist in penetration of the slurry between the faying surfaces of an assembly.
- 5 The present process finds exceptional utility in the production of heat exchanger assemblies, such as oil coolers for motor vehicles.
- As already stated, the flux consists essentially of a mixture of potassium fluoaluminates, essentially free of unreacted potassium fluoride. As herein used, "potassium fluoaluminate" refers to substances of the type formed by fusion of AlF_3 and KF , such complexes having the formulae K_3AlF_6 and KAIF_4 . X-ray diffraction examination of the solidified residue of the fused eutectic mixture of KF and AlF_3 , which occurs at about 45.8% KF and 54.2% AlF_3 , indicates that virtually all the fluoride contents are in the form of K_3AlF_6 and KAIF_4 , which are very sparingly soluble in water and are non-hygroscopic. The fused eutectic consists of these two phases and is virtually free of KF and AlF_3 .
- The liquidus point of a mixture of potassium fluoaluminates varies depending upon the composition of the mixture, expressed as relative proportions of AlF_3 and KF , reaching a minimum (about 560°C) at the aforementioned eutectic composition and it is accordingly preferred to employ a flux which complies closely with the eutectic composition. However, other flux compositions within the broader composition limits stated in our Patent No. 1,438,955 are also suitable in the process of the present invention. While the flux melting point shown in the published diagram (Journal American Ceramic Society, 49, pages 631—34, December 1966) rises very rapidly if the quantity of KF rises above that required for the eutectic, there is only a slight rise in melting point to about 574°C where the AlF_3 rises above the eutectic up to a total of about 60% (50 mole % AlF_3). For aluminium brazing operations, it is commonly preferred that the AlF_3/KF ratio of the potassium fluoaluminate be such that the flux becomes reactive at not more than 600°C. Preferably, the flux is an intimate mixture of K_3AlF_6 and KAIF_4 , corresponding to an AlF_3/KF ratio between 60:40 and 50:50, in parts by weight, essentially free of unreacted KF .
- At compositions corresponding to an AlF_3 content below 60%, the mixture of potassium fluoaluminate complexes, in the dry state, consists essentially of K_3AlF_6 and KAIF_4 . At higher levels of AlF_3 content within the stated range, the mixtures are constituted of KAIF_4 with some unreacted AlF_3 (which is insoluble in water) but,
- again, essentially free of unreacted KF . Minor amounts of other fluorides (e.g. LiF , NaF or CaF_2) may be incorporated in the flux.
- Because the potassium fluoaluminate flux does not deleteriously attack brazing alloy powder when mixed in water, the powdered flux-alloy bath has a useful life of several days or longer, whereas the use of a conventional chloride flux in such a bath would have a short life owing to attack on the brazing alloy by the chlorides. Indeed, it is found that a slurry in accordance with the present invention can be rejuvenated by a 10% weight addition of the flux and brazing alloy powder in the desired proportions.
- Various additions may be made to the aqueous slurry of flux and brazing alloy powders without departing from the present invention. For example, conventional surfactants, thickeners and/or dispersing agents may be employed. In practice, however, satisfactory results have been achieved without any of these additives.
- EXAMPLE I
- One hundred parts by weight of -200 mesh size Al-12% Si brazing alloy powder and 25 parts by weight of -200 mesh size potassium fluoaluminate powder (a mixture of KAIF_4 and K_3AlF_6) were mixed with 75 parts by weight of deionized water and maintained in suspension in the resulting slurry by mechanical stirring. (Mesh Numbers are U.S. Sieve Series). Small specimens of cleaned aluminium, 2.5 cm x 2.5 cm, were dipped in the mechanically stirred slurry and withdrawn at a rate such that a uniform deposit of flux and metal powder remained on the surfaces of the specimens. After drying, the coating of flux and brazing alloy powder was removed from all but one surface of each specimen. Coating weights ranging from 30 to 180 grams per square metre were produced in this way, merely by varying the consistency of the slurry by dilution with water. Each specimen was successfully brazed to uncoated specimen in a tube furnace having an atmosphere of dry nitrogen.
- EXAMPLE II
- A slurry was prepared consisting of 4 grams of the potassium fluoaluminate flux powder, 160 grams of the Al-Si brazing alloy powder, and 108 ml of de-ionized water. This slurry was applied to surfaces of aluminium samples so as to achieve a coating weight (after drying) of 135 grams per square meter. Fully effective brazing was achieved with the samples thus coated, although the metal/flux ratio in this instance was 40:1.

EXAMPLE III

A slurry consisting of 10 parts Al-10% Si brazing alloy powder and 1 part of flux (the eutectic mixture of $KAlF_4$ and K_3AlF_6) was mixed with sufficient water to provide, after immersion of plates of aluminium alloy designated AA3003 intended to form an oil cooler heat exchanger, in the air agitated slurry, dry coating weights ranging from 45 to 135 g/sq. metre. The plates were racked while still wet. Uncoated end plates were used; the brazing alloy of the slurry on the exterior heat exchange plates provided the filler metal for brazing the end plates. After assembly, the unit was dried at 200°C for 5 minutes, then placed in a furnace filled with dry nitrogen. The unit was heated to a temperature of 590°C over a 12-minute period and allowed to cool to 550°C before removal from the furnace. After cooling to room temperature, the parts were pressure tested using compressed air at 20 psig. No leaks were detected with those units with a solids coating weight of 70 g/sq. metre or more.

WHAT WE CLAIM IS:—

1. A method of joining aluminium components by means of an aluminium brazing alloy having a melting point lower than that of the aluminium components, in which the assembled components are heated to a temperature above the melting point of the brazing alloy and below the melting point of said components in the presence of a potassium fluoaluminate flux, which is essentially free of unreacted KF

characterised in that the flux and the brazing alloy are applied to the surface of at least one of the components as aqueous slurry of finely divided flux and metal power, the film of slurry is then dried and the components are brazed by heating in a dry, oxygen-free inert gas atmosphere, the application of flux/brazing alloy slurry being controlled to apply 30—180 gms/m² of solids and the flux: brazing alloy ratio being selected to deposit at least 3.29 gms/m² of flux.

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2. A method according to claim 1 further characterised in that the ratio of brazing alloy powder to flux in said slurry is in the range of 4-40:1.

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3. A method according to claim 1 or 2 further characterised in that the brazing alloy/flux mix is deposited by immersing said one component into a bath of said slurry.

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4. A method according to claim 1 or 2 further characterised in that the assembled components are dipped into a bath of said slurry to deposit the brazing alloy/flux mix between the faying surface of said assembled components.

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5. A method according to any of claims 1 to 4 further characterised in that the inert gas is nitrogen.

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